



Why palladium cathodes can bear resistance to methanol but not platinum cathodes



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ABSTRACT

Methanol crossover on the cathodes causes significant performance loss in direct methanol fuel cells, and the parasitic current induced by the electrochemical oxidation of methanol on the cathodes is believed to be the cause. Palladium cathodes are known to bear resistance to methanol but not platinum cathodes. By means of the density functional theory (DFT), the distorted molecular structure of the adsorbed methanol on platinum was revealed, and this distorted molecular structure indicates that platinum makes methanol has a tendency toward the elimination of the first hydrogen (involved in the first step of electrochemical oxidation of methanol) in electric neutrality, and loss of an electron can reinforce this tendency. However, palladium cannot distort the molecular structure of the adsorbed methanol, even in the loss of electron condition. The activation energies and the reaction energies calculated by means of DFT also show that after losing an electron, the elimination of the first hydrogen on platinum is more kinetically and thermodynamically favourable than that on palladium. These computational results can explain the experimental findings that no parasitic current is induced at palladium cathodes, but not at platinum cathodes; therefore, palladium cathodes have a methanol-resistance property.

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1. Introduction

The direct methanol fuel cells (DMFCs) usually operate in acidic electrolytes with platinum-containing anode and cathode catalysts. In DMFCs, methanol is used as a fuel and oxidized at anodes, while oxygen is reduced at cathodes. These DMFCs have the problem of methanol crossover on the platinum cathodes, causing significant performance loss [1,2]. The parasitic current at the platinum cathodes due to electrochemical oxidation of methanol as well as adsorption of methanol and its oxidized species on the platinum cathodes reduce the amount of electrons flowing from the anodes to the cathodes [3]. One of the solutions is to seek other cathode catalysts, which are resistant to methanol.

It is known that palladium cathodes bear resistance to methanol but not platinum cathodes. However, the electrochemical oxygen reduction activity of palladium is lower than that of platinum. Therefore, it motivates many researchers to devote on synthesizing different palladium alloys in order to raise the electrocatalytic activity of oxygen reduction. Recent reviews report various kinds of palladium-based cathode catalysts including Pd,

Pd-Fe, Pd-Ni, Pd-Ni-Se, Pd-Co, Pd-Co-Mo, Pd-Ti, Pd-Cr, Pd-Ta, Pd-Cu and Pd-Au [4–6]. In addition, the dissolution of palladium occurs at higher positive potentials in acidic electrolytes; [7,8] therefore, alloying gold with palladium-based catalysts has been proposed to improve the stability [9]. Alternatively, the palladium content in the Pd/C gas diffusion electrode can increase, leading to its activity of the electrochemical reduction of oxygen comparable to that of the Pt/C gas diffusion electrode, and the cost will not be greatly affected as the price of palladium is several times lower than that of platinum [5,6]. Also, pure palladium may bear higher corrosion resistance in acidic electrolytes when compared with palladium alloyed with non-precious metals according to the phenomenon of preferential dissolution of less noble components in alloys [10].

It is believed that the parasitic current induced by electrochemical oxidation of methanol at the Pt cathodes is the cause of performance loss [11,12]. The cyclic voltammograms show that there is no electrochemical oxidation of methanol at Pd electrodes in HClO₄, even in solutions saturated with O₂, but not at Pt electrodes, [13] implying no parasitic current at Pd cathodes. From the polarization curves for the electrochemical reduction of oxygen, the methanol causes 26% drop in the open circuit potential for the Pt/C gas diffusion electrode pressurized with O₂, while around 7% decrease in the open circuit potential for the Pd/C gas diffusion electrode results from the presence of methanol [13]. In

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addition, the decrease in the current density caused by the methanol for the Pt/C gas diffusion electrode is greater than that for the Pd/C gas diffusion electrode [13]. Therefore, the small decreases in the open circuit potential and the current density for the Pd/C gas diffusion electrode are mainly attributed to the competitive adsorption of methanol on the Pd electrode surface rather than the parasitic current.

The aim of the current study is to provide theoretical explanations why palladium cathodes can bear better resistance to methanol but not platinum cathodes. Thus, DFT [14,15] was adopted to describe the parasitic current generated by the electrochemical oxidation of methanol at platinum and palladium cathodes. The induction of the parasitic current or not can be explained by the following DFT data concerning the structures of the adsorbed CH₃OH molecule on single layers of the Pt and Pd lattices, which are composed of 13 atoms (Pt₁₃⋯CH₃OH and Pd₁₃⋯CH₃OH), in the conditions of electric neutrality and loss of an electron, and the DFT results below related to the activation energies and the reaction energies of the elimination of the first H atom from the adsorbed CH₃OH molecule after losing an electron that is involved in the first step of electrochemical oxidation of methanol.

2. Results and Discussion

After geometry optimization, the CH₃OH molecule can express two orientations on the Pt and Pd lattices: orientation 1 – one of the H atoms on the C atom pointing toward the lattices (Figs. 1a and b); orientation 2 – the O atom pointing toward the lattices (Figs. 2a and b). These two respective orientations are consistent with the orientations of the first adsorbed species on electrodes in the two proposed mechanisms of electrochemical oxidation of methanol: mechanism 1 – the successive removal of the H atoms on the neighboring C atom followed by the H atom on the neighboring O atom; [16,17] mechanism 2 – the removal of the H atom on the neighboring O atom with the subsequent elimination of the H atoms on neighboring the C atom [16,17]. The following equations are the first steps of these two mechanisms.

First step of mechanism 1: M-H-CH₂OH (orientation 1) → M-CH₂OH + H⁺ + e⁻

First step of mechanism 2: M-OH(CH₃) (orientation 2) → M-OCH₃ + H⁺ + e⁻

where M: metal electrode surface.

Regarding the orientation 1, in the Pt-H-CH₂OH, the distance between the Pt atom and the H atom pointing toward the Pt lattice is 1.94 Å (Fig. 1a) which is significantly shorter than the distance between the Pd atom and the corresponding H atom in the Pd-H-CH₂OH (2.29 Å; Fig. 1b). The bond between the C atom and

the H atom pointing toward the Pt lattice is elongated to 1.17 Å in the Pt-H-CH₂OH (Fig. 1a), weakening the C-H bond; however, the corresponding C-H bond length in the Pd-H-CH₂OH is 1.10 Å (Fig. 1b), which is the same as the bond length of C-H in the free CH₃OH molecule (Fig. 3). The results imply stronger adsorption of the CH₃OH molecule staying in the orientation 1 on Pt than Pd. Therefore, Pt can weaken the C-H bond and facilitate the elimination of the H atom on the C atom, but not Pd, when electrochemical oxidation of methanol follows the mechanism 1.

Since the first step of electrochemical oxidation of methanol involves loss of an electron, the adsorbed CH₃OH molecule on the Pt and Pd lattices carrying a positive charge before complete elimination of the first H atom were examined. From Fig. 4a, the adsorbed CH₃OH molecule remains in the orientation 1: [Pt-H-CH₂OH]⁺ after geometry optimization. The loss of an electron can shorten the distance between the Pt atom and the H atom further (from 1.94 Å (Fig. 1a) to 1.80 Å (Fig. 4a)), and the bond length of the corresponding C-H increases more (from 1.17 Å (Fig. 1a) to 1.22 Å (Fig. 4a)). The results reflect that the loss of an electron can strengthen the adsorption of the CH₃OH molecule staying in the orientation 1 on Pt, further weakening the C-H bond. Therefore, the loss of an electron can assist in the removal of the H atom on the C atom in the CH₃OH molecule adsorbed on Pt when the mechanism 1 is obeyed. Unlike the Pt system, no optimized structure of [Pd-H-CH₂OH]⁺ was found during geometry optimization. This is because even though the starting geometry for geometry optimization was based on the orientation 1, the orientation of the optimized structure of the adsorbed CH₃OH molecule on Pd changed to 2 (Fig. 4b) when carrying a positive charge. It implies that after losing an electron, the adsorbed CH₃OH molecule on Pd moves from the orientation 1 to the orientation 2.

Pd-H-CH₂OH (orientation 1) → [Pd-OH(CH₃)]⁺ (orientation 2) + e⁻

For the orientation 2, the distance between the Pt atom and the O atom in the Pt-OH(CH₃) (2.35 Å; Fig. 2a) is longer than that between the Pd atom and the O atom in the Pd-OH(CH₃) (2.28 Å; Fig. 2b). The DFT data show that the bond lengths of the O-H in the Pt-OH(CH₃) (Fig. 2a), the Pd-OH(CH₃) (Fig. 2b) and the free CH₃OH molecule (Fig. 3) are almost the same (0.97–0.98 Å). After losing an electron, the distance between the Pt atom and the O atom in the [Pt-OH(CH₃)]⁺ becomes shorter (2.23 Å; Fig. 4c); however, the bond length of the O-H in the adsorbed CH₃OH molecule (0.98 Å; Fig. 4c) is still insignificantly different from that in the free CH₃OH molecule. In the [Pd-OH(CH₃)]⁺, the bond length of the O-H in the adsorbed CH₃OH molecule (0.97 Å; Fig. 4b) is the same as that in the free CH₃OH molecule. Also, the distance between the Pd atom and the O atom (2.26 Å; Fig. 4b) in the [Pd-OH(CH₃)]⁺ still has no significant change when compared with that in the [Pd-OH(CH₃)]. The results indicate weak adsorption of the CH₃OH molecule staying in the orientation 2 on Pt and Pd in the conditions of electric neutrality and loss of an electron, resulting in low tendency

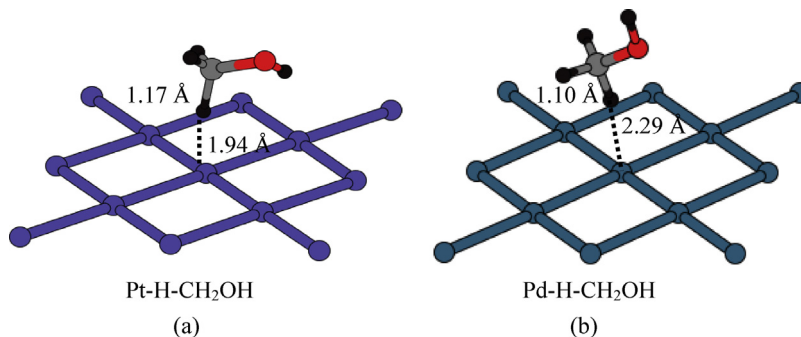


Fig. 1. Optimized structures of the adsorbed CH₃OH molecule staying in the orientation 1 on (a) the Pt lattice and (b) the Pd lattice.

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